



# Contaminants Assessment of Intertidal Resources in Southeast Alaska National Parks—2007 to 2011

Natural Resource Technical Report NPS/SEAN/NRTR – 2012/630



**ON THE COVER**

R/V Capelin, captained by Justin Smith, in Glacier Bay National Park on a typical sunny day.  
Photograph: David A. Tallmon

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# **Contaminants Assessment of Intertidal Resources in Southeast Alaska National Parks—2007 to 2011**

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## Abbreviations

ADFG	Alaska Department of Fish and Game
As	arsenic
Ca	cadmium
CHLD	chlordanes
DDT	dichloro diphenyl trichloroethanes
GLBA	Glacier Bay National Park and Preserve
HCH	hexachlorocyclohexanes
Hg	mercury
KLGO	Klondike Gold Rush National Historical Park
LOQ	limits of quantitation
MWP	Mussel Watch Program
NOAA	National Oceanic and Atmospheric Administration
NPS	National Park Service
PAH	polycyclic aromatic hydrocarbons
PBDE	polybrominated biphenyl ethers
PCB	polychlorinated biphenyls
POP	persistent organic pollutants
ppb	parts per billion
TBT	tributyltin
TPAH	total polycyclic aromatic hydrocarbons
SEAN	Southeast Alaska Network
SITK	Sitka National Historical Park
UAS	University of Alaska Southeast

## Executive Summary

Glacier Bay National Park and Preserve (GLBA), Klondike Gold Rush National Historic Park (SITK), and Sitka National Historic Park (SITK) form the network of US National Parks in Southeast Alaska (SEAN). The purpose of this report is to provide the results of a rigorous baseline assessment of existing contamination levels in the SEAN parks. Intertidal bay mussel samples were collected at a large number of sites in and near each of the parks in July and August 2007. At some of the same sites, sediment samples were also collected. Additional mussel samples were collected from six sites in GLBA and SITK in both 2009 and 2011. The samples were analyzed to determine levels of several metals, polycyclic aromatic hydrocarbons (PAH), and persistent organic pollutants (POP) in SEAN parks. Overall, marine contamination levels in and around SEAN parks are low. Although there are a few sites at which contamination levels are elevated, these sites are close to centers of human activity and potential point sources. The overall patterns of contamination suggest most of the impacted sites are affected primarily by local, rather than regional or global sources. However, the low levels of contamination in mussels throughout SEAN parks suggest the intertidal zones are relatively pristine when compared to mussel contaminants datasets from the rest of the US.



# Introduction

Seemingly pristine and protected areas can be negatively impacted by contaminants from extremely distant, as well as nearby, sources. Contaminants take many forms and threaten a variety of different components and trophic levels of ecosystems. Research in the last few decades has shown that some contaminants can reach high latitudes from distant sources via different transport mechanisms and can accumulate through food webs, threatening the health of top predators and humans (MacDonald et al. 2003, AMAP 2004).

In Southeast Alaska, recent research has shown that contaminants from a wide range of sources are a serious concern, even though the Gulf of Alaska is among the most pristine marine ecosystems yet tested for contaminants (Wright et al. 2000). A comprehensive study of western US national parks found that GLBA had higher levels of some POP in terrestrial vegetation than many other parks (Landers et al. 2008). In addition, a recent study of walleye pollock (*Theragra chalcogramma*), found higher levels of some POP in fish collected in Southeast Alaska than the same species collected from the Bering Sea (Heintz et al. 2006).

SEAN parks potentially face both local and global contamination threats (Engstrom and Swain 1997, Landers et al. 2008). There is increasing evidence from a broad array of studies that point and non-point source pollution created at relatively warm, low latitudes can be transported to relatively colder, higher latitudes via the “grasshopper effect”, in which pollution vaporizes at the relatively higher temperatures found at low latitudes and is carried in the atmosphere before condensing at lower temperatures found at high latitudes and being deposited onto land or water (AMAP 2004). Consequently, northern regions can have surprisingly high levels of some contaminants that are not broadly discharged or created in the region. There is also evidence that some parts of Alaska have accumulated moderate levels of some heavy metals, and other contaminants, such as POP and PAH (Hurwich and Chary 2000, Gabrielsen et al. 2003). Some of these contaminants have been detected in sediment and water samples, and have bioaccumulated in marine and freshwater organisms. Locally, heavy daily and seasonal boat traffic within or near SEAN park boundaries make oil spills or spills of other contaminants a risk.

In protected places such as national parks, where resource management budgets and access are typically limited, it is important to think critically about contaminants relative to the threat they pose, their modes of transport, how they can best be assessed and monitored, and at what levels they must be detected. It is impossible to know with certainty what future threats SEAN parks will face, in part because global economic trends and regulations on contaminants will greatly affect their delivery to Alaska. However, existing information provides useful insights into likely threats to SEAN parks. Previous studies of SEAN parks have identified marine vessels and atmospheric (non-point) sources as the most likely contributors of contaminants to these protected areas (Eckert et al. 2006b, a, Hood et al. 2006). It has been suggested in a variety of studies (reviewed by MacDonald et al. 2003) that Asian atmospheric pollutants could easily pollute western North America due to prevailing wind and deposition patterns.

A major management objective of SEAN parks is the assessment of current contaminant levels in the parks and whether these levels should be of concern. This study is motivated by the desire to

gain a baseline inventory of contaminant levels for reference against future conditions or in case of a catastrophic event, such as a major oil spill. Considering that a large number of different analytes could be sampled from several different trophic levels and abiotic media (including air, sediments, and water) in a number of different ecosystems (freshwater, marine, terrestrial), that lab costs for determining a suite of contaminants are expensive, and that inferences should be made at both the park and network spatial scales, careful attention was given to exactly what should be sampled to assess contaminant levels. Indeed, the NPS has moved to standardize, document, and maximize the information produced and design of all of its assessment and monitoring programs (Oakley et al. 2003).

Given these considerations and the diversity of potential sampling regimes, a number of explicit objectives were crafted for this study to reflect the contaminant assessment goals of SEAN parks:

- Make spatially balanced and rigorous inferences at the park and network spatial scales.
- Select analytes most likely to be current or future contaminant threats to SEAN parks.
- Select samples and ecosystems that are most susceptible to these contaminant threats.
- Select a target organism that likely integrates contaminant levels over time.
- Select a parameter or analyte that can be compared with existing benchmarks or criteria, or contaminant loads from other areas in order to put the existing levels in perspective of ‘healthy ecosystems’.
- Select samples that will minimize any conflict with the NPS mandates of non-invasive sampling and wilderness conditions.
- Sample an organism that integrates contaminants over time yet reflects the contaminant loads within the parks, i.e., is not a function of migration from outside areas.

To meet the majority of these objectives within the funding and logistical constraints on sampling, the bay mussel (*Mytilus trossulus*) was chosen as the target species to sample marine contaminants. It was determined that mussels provide the best ability to make external and internal inferences from data, offer relatively inexpensive sampling costs, and yield insight into chronic, as well as potential catastrophic, contamination threats. This report contains the results from efforts to obtain baseline contaminant information for each of the three parks using bay mussels as the target organism.

A primary benefit of using contaminant levels from mussels to make inferences about park health is that these levels can be compared to an existing database collected as part of the national Mussel Watch Program (MWP), which is responsible for monitoring over 100 contaminants in mussel tissue collected at over 280 sites since 1986 and maintains the longest running contaminants sampling program in the US (O'Connor 2001). The MWP program recently completed a report detailing 20 years of data, including five MWP sites in the Gulf of Alaska and Southeast (Kimbrough et al. 2008). One of these sites is near KLGO. This is important because a vital component of any park inventory program is the ability to make inferences about conditions at park sample sites relative to one another, and to areas outside the park. These inferences make it possible to determine whether contaminant sources are most likely local, regional, or global. In turn, this information greatly facilitates identification of specific sources, mechanisms of contamination, and the means to minimize or mitigate contaminant threats. Because of the MWP, mussels collected and analyzed in a manner

consistent with MWP protocols will meet a universal goal in contaminant assessment studies of providing data that can be compared to similar data collected outside the sampling area to obtain valid internal and external inferences.

In addition, because funding is limited, it was necessary to obtain data from something relatively inexpensive to collect. The costs of contaminant lab analyses run a minimum of several hundred dollars per sample per class of analytes. Due to this high “front-end” cost that cannot be avoided, it was important to minimize other costs associated with obtaining samples. Obtaining tissue samples from large, mobile, high trophic-level organisms, such as marine mammals, is often time-intensive, expensive, and controversial. This can all lead to limited sample sizes. In contrast, mussels can be obtained relatively quickly and cheaply, which makes it possible to obtain large sample sizes.

Furthermore, mussels are useful contaminants study organisms because they are sessile filter feeders and live up to 20 years, providing insight into contamination that has occurred over the previous several years, as well as indicating any recent catastrophic events in nearby areas. Mussels bioaccumulate and bioconcentrate many contaminants. However, unlike highly migratory species such as marine mammals, mussels are not likely to provide misinformation about park contamination status as a result of contamination occurring elsewhere.

Marine contaminants have been identified as important threats to park integrity in recent water quality reports (Eckert et al. 2006b, a, Hood et al. 2006). The intertidal contaminant assessment of samples collected in 2007 compliments these efforts to obtain baseline data on the extent and types of intertidal resources via recent mapping efforts (*e.g.*, Coastwalker or ShoreZone). The objectives of this effort are to provide a comprehensive assessment that includes maps of sampling sites and results from contaminant analyses of samples from each park or nearby shoreline. This report includes a synthesis of existing literature and context for the results from SEAN parks with respect to local, regional, and global contamination threats and trends. In addition, all results will be archived into a database that includes GPS coordinates, site descriptions, and contaminant levels from SEAN parks and nearby comparison sites. This will serve as a valuable baseline to make inferences about future trends in contaminants and as a reference should any catastrophic events occur. Resampling in 2009 and 2011 at a limited number of sites also provides insights into the temporal stability of the 2007 baseline samples. Finally, a sampling protocol for long-term monitoring of park contaminants was developed that matches very closely with the MWP sampling protocol, and should make it easier to have these SEAN park sites adopted into MWP sampling efforts in the near future.

## Methods

### Sampling Design

Sampling effort was allocated based somewhat upon political boundaries, perceived high risk areas, and geographic constraints. To ensure broad inferences could be made about all parks within SEAN, samples were collected from all three parks and/or nearby areas. Due to their smaller sizes and shorelines, fewer samples were collected in and around KLGO and SITK relative to GLBA. Whenever possible, “hot control” sites of relatively heavy human use, and located within or near park boundaries, were included in the sampling effort to help contextualize randomly sampled locations and provide insights into whether any contamination is a regional or local phenomenon. At KLGO, mussel samples were collected near the Taiya River outlet and the mouth of the Skagway small boat harbor. At SITK, samples were collected from Crescent Harbor, in front of the Visitor’s Center, and near the mouth of the Indian River.

Because of its large area, GLBA was divided into five strata: Icy Strait/Outer Coast, Lower Bay, East Arm, West Arm, and Bartlett Cove. Sites within each stratum were randomly selected using a Coastwalker GIS layer that contains the entire distribution of mussels in GLBA broken into small linear segments of shoreline. In each stratum, segments were randomly selected from the total number of shoreline segments containing mussels. The midpoint of each randomly selected segment was designated a potential target sample site.

From the potential target sample collection sites in Figure 1, a subset were randomly selected and sampled. In each of the five GLBA strata, except Bartlett Cove, nine randomly selected sites were sampled. Only three randomly selected sites were sampled in Bartlett Cove, due to its small size. Using this approach we obtained a geographically diverse and representative sample of intertidal mussels and contaminants. The locations of all sites sampled in 2007, including both GPS coordinates and general descriptors, are provided in Table 1. All 2007 samples begin with the numbers 1801---

As mentioned above, samples were collected from several non-randomly selected, potentially contaminated sites, so that we could have “hot” controls for comparison to sites thought to be relatively more pristine. These controls sites include the boat harbors adjacent to SITK and KLGO, a boat dock at outer Elfin Cove, the fueling dock in Bartlett Cove, the Bartlett Cove boat ramp, and the beach next to the effluent from the Excursion Inlet fish processing plant.

In both 2009 and 2011, six sites were re-sampled from GLBA and SITK using the 2007 sampling protocol described below. These samples provide insights into the temporal stability of the 2007 assessment and a means to identify any dramatic contamination events. The 2009 and 2011 samples can be found at the bottom of each table and begin with the numbers 2009-- and 2011--, respectively.

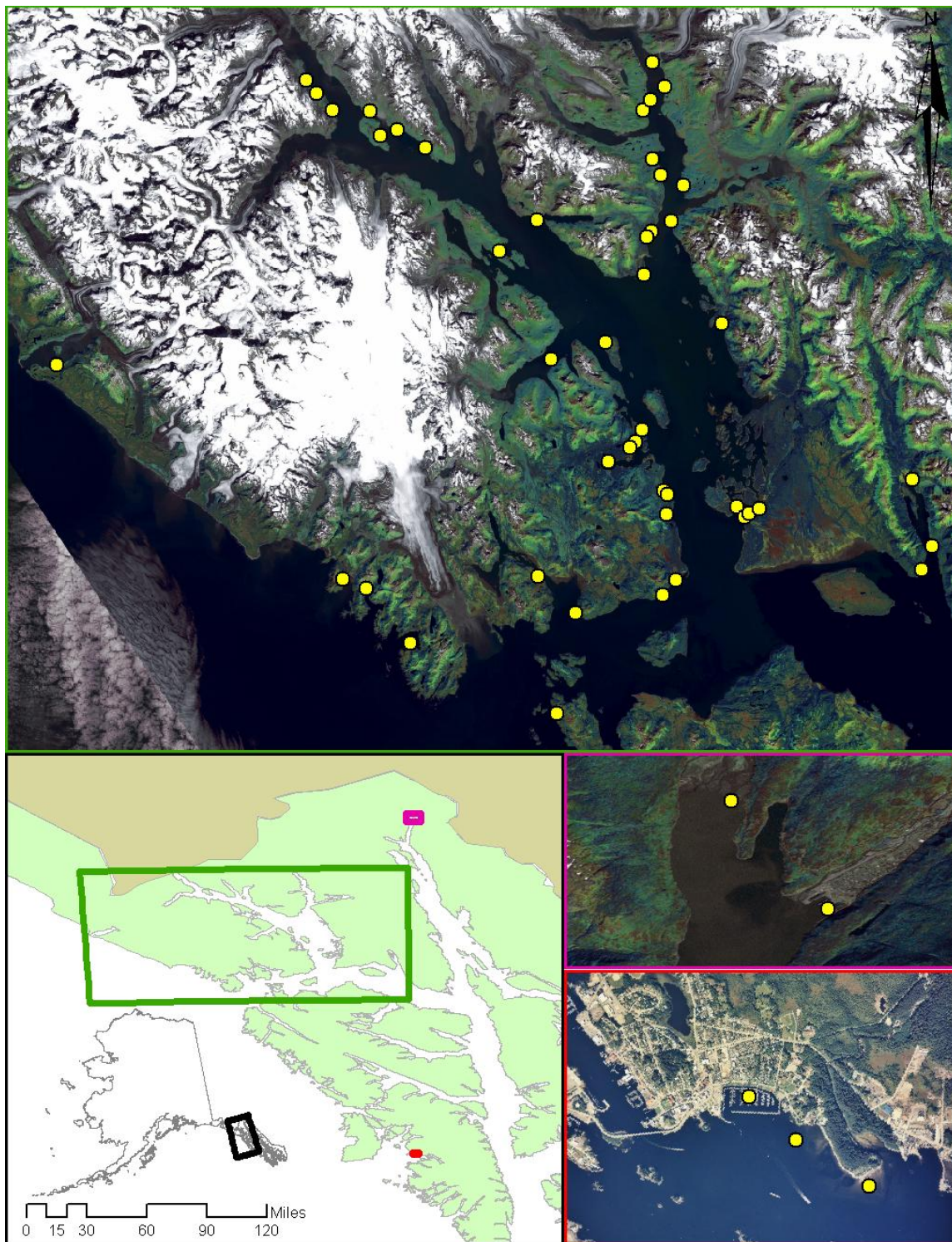
### Collection Protocol

Between July 23, 2007, and August 29, 2007, each of the identified 2007 sample sites was approached by boat, foot, or floatplane, and sampled as nearby as possible. Although every reasonable effort was made to sample the exact location identified in the list of sample sites, this

was sometimes not possible due to difficulty in landing or walking to the site. The GPS location of each sample was obtained with a handheld GPS unit and all sample site coordinates are contained in Table 1 as decimal degrees latitude and longitude. However, GPS coordinates were not collected for samples 1801640 and 1801650 at the time of collection, so these were obtained using GoogleEarth after sampling. GPS coordinates were not collected for the samples 201105 and 201106, and could not be identified after sampling because the collector retired from the NPS before these data could be obtained. All 2007 sample sites in and nearby each SEAN park are shown in Figure 1. Between August 4 and September 1, 2009, additional mussel samples were collected from six of the sites sampled in GLBA and SITK in 2007. These six sites were re-sampled between August 10 and September 6, 2011.

Mussels were collected near low tide in accordance with the protocols developed by MWP (Appendix A). At each site, the time, water temperature, height of collection above the water level, GPS location, and the height of the highest mussel distribution relative to water level were noted. Individual mussels were collected from multiple clumps of mussels until at least 35 grams wet weight was obtained. This corresponded to approximately 30-60 mussels per site, depending upon individual mussel size. The sample from each site was then divided into three new Ziploc bags. Each sample bag was uniquely labeled on the outside using a Sharpie marker. A piece of Rite-in-the-Rain waterproof paper with the sample number was also placed inside each bag as an additional identifier. The only departures in the mussel collection protocol employed here from that of the MWP are that salinity levels were not recorded and wet weights were reported for each contaminant.

At some of the sites, both mussels and sediments were collected. The sediment collection protocol follows procedures developed by Larry Holland (NOAA TSMRI, Juneau, AK). Sediment was collected into 250 ml iChem certified clean glass jars using a treated stainless steel spoon. Each spoon was treated in the lab using a 10% HCl and acetone treatment. Next, each spoon was individually wrapped in aluminum foil and stored in a clean, unused Ziplock bag until used. Immediately before use, each spoon was rinsed in seawater and then used to scoop sediment into an iChem certified clean glass jar. Each spoon was used only once and each of the sediment sample jars was uniquely labeled.



**Figure 1.** Sample site locations in each of the SEAN parks. The SEAN region is shown in the lower left panel. Yellow dots on each of the other panels indicate sample sites within and nearby each park (upper=GLBA, middle = KLGO, bottom=SITK).



**Table 1.** Mussel and sediment sample numbers, sample type, site descriptions, and locations in SEAN parks and nearby areas. 2007 sample numbers begin with '1801', 2009 with '2009', and 2011 with '2011.'

Sample	Type	Park	Site Description	Latitude	Longitude
1801601	Mytilus	KLGO	Dyea	59.47942	-135.34752
1801602	Mytilus	KLGO	Skagway Harbor*	59.44890	-135.32188
1801603	Mytilus	GLBA	Berg Bay	58.51654	-136.23077
1801604	Mytilus	GLBA	Berg Bay	58.54318	-136.16562
1801605	Mytilus	GLBA	Berg Bay	58.53614	-136.17885
1801606	Mytilus	GLBA	Bartlett Cove	58.46268	-135.91751
1801607	Mytilus	GLBA	Bartlett Cove	58.44944	-135.89943
1801608	Mytilus	GLBA	B Boat Ramp*	58.45421	-135.88731
1801609	Mytilus	GLBA	Ripple Cove	58.45203	-136.08733
1801610	Mytilus	GLBA	N Rush Point	58.48175	-136.09517
1801611	Mytilus	GLBA	S Whidbey Psg	58.55906	-136.15013
1801612	Mytilus	GLBA	N Drake Island	58.66893	-136.24503
1801613	Mytilus	GLBA	Geikie Inlet Isl	58.64629	-136.37547
1801614	Mytilus	GLBA	Sebree Island	58.75578	-136.15181
1801615	Mytilus	GLBA	N Caroline Pt	58.81132	-136.13606
1801616	Mytilus	GLBA	Muir Pt	58.82409	-136.08734
1801617	Mytilus	GLBA	N Pt George	58.86981	-136.06041
1801618	Mytilus	GLBA	Gateway Knob	58.88284	-136.11569
1801619	Mytilus	GLBA	Hunters Cove	58.90239	-136.13593
1801620	Mytilus	GLBA	Spokane Cove	58.69488	-135.96101
1801621	Mytilus	GLBA	B Fuel Dock*	58.45483	-135.88855
1801622	Mytilus	GLBA	Bartlett R Trib	58.46094	-135.86191
1801623	Mytilus	GLBA	S Stump Cove	58.96441	-136.16190
1801624	Mytilus	GLBA	Westdahl Pt	58.97733	-136.14368
1801625	Mytilus	GLBA	N Nunatak Cr	58.99449	-136.10962
1801626	Mytilus	GLBA	McBride Spit S	59.02553	-136.14200
1801627	Sediment	GLBA	McBride Spit S	59.02553	-136.14200
1801628	Mytilus	GLBA	Tidal Inlet	58.82209	-136.41751
1801629	Mytilus	GLBA	E Russell Rocks	58.91086	-136.69583
1801630	Mytilus	GLBA	Russell Fan	58.93266	-136.76550
1801631	Mytilus	GLBA	Russell Island	58.92451	-136.80803
1801632	Mytilus	GLBA	N Russell Fan	58.95527	-136.83455
1801633	Mytilus	GLBA	S Tarr Inlet	58.95572	-136.92593
1801634	Mytilus	GLBA	Tarr Inlet	58.97688	-136.96820
1801635	Mytilus	GLBA	W Hazelton Camp	58.99239	-136.99268
1801636	Mytilus	GLBA	Blue Mouse Cove	58.78226	-136.50848
1801637	Sediment	GLBA	Blue Mouse Cove	58.78226	-136.50848
1801638	Mytilus	GLBA	Upper Excursion	58.49899	-135.49251
1801639	Sediment	GLBA	Upper Excursion	58.49899	-135.49251
1801640	Mytilus	GLBA	Excursion Fish Plt*	58.41500	-135.44411
1801641	Mytilus	GLBA	Lower Excursion	58.38483	-135.46693
1801642	Mytilus	GLBA	NE Pleasant Island	58.37670	-135.60751
1801643	Mytilus	GLBA	E Carolus R	58.36835	-136.06175
1801644	Sediment	GLBA	E Carolus R	58.36835	-136.06175
1801645	Mytilus	GLBA	W of Carolus	58.34905	-136.09467

Table 1. (continued) Mussel and sediment sample numbers, sample type, site descriptions, and locations in SEAN parks and nearby areas.

Sample	Type	Park	Site Description	Latitude	Longitude
1801646	Mytilus	GLBA	W Pt Dundas	58.32486	-136.30461
1801647	Sediment	GLBA	W Pt Dundas	58.32486	-136.30461
1801648	Mytilus	GLBA	W Arm Dundas	58.36961	-136.39734
1801649	Mytilus	GLBA	Outer Elfin Cove*	58.19550	-136.34578
1801650	Mytilus	GLBA	Mouth Rush Pt Cr	58.47543	-136.08991
1801701	Mytilus	GLBA	Graves	58.28159	-136.70290
1801702	Mytilus	GLBA	Torch Bay N	58.3492	-136.81209
1801703	Mytilus	GLBA	Dixon Harbor	58.35973	-136.86961
1801704	Mytilus	GLBA	Lituya Bay	58.62025	-137.58104
1801705	Mytilus	SITK	Visitor's Center	57.04777	-135.31777
1801706	Mytilus	SITK	Indian R	57.04476	-135.31116
1801707	Mytilus	SITK	Crescent Harbor*	57.05065	-135.32668
1801708	Mytilus	GLBA	Berg Bay	58.51742	-136.23083
1801709	Sediment	SITK	Visitor's Center	57.04777	-135.32055
200901	Mytilus	GLBA	E Russell Rocks	58.91089	-136.69597
200902	Mytilus	GLBA	W Hazelton Camp	58.99259	-136.99287
200903	Mytilus	GLBA	Ripple Cove	58.45261	-136.08752
200904	Mytilus	GLBA	Bartlett Cove	58.44944	-135.89943
200905	Mytilus	SITK	Visitor's Center	57.04780	-135.32060
200906	Mytilus	SITK	Crescent Harbor*	57.05070	-135.32670
201101	Mytilus	GLBA	E Russell Rocks	58.91107	-136.69620
201102	Mytilus	GLBA	W Hazelton Camp	58.99271	-136.99306
201103	Mytilus	GLBA	Ripple Cove	58.45086	-136.08684
201104	Mytilus	GLBA	Bartlett Cove	58.44984	-135.89995
201105	Mytilus	SITK	Visitor's Center	NA**	NA**
201106	Mytilus	SITK	Crescent Harbor*	NA**	NA**

\* "hot" control site as described in the text.

\*\* NA = not available.

Mussel and sediment samples were immediately placed in a cooler following collection. They were frozen upon return from each daily sampling trip and kept frozen until shipped to the appropriate lab for contaminant analysis. Frozen samples were shipped in labeled coolers containing ice kept in separate, sealed bags to prevent opening and contamination of mussel samples. By using this sampling scheme to obtain samples and by analyzing a large suite of contaminants in these samples, we obtained a broad picture of contamination levels in SEAN parks and nearby intertidal areas.

### Lab Analyses

The samples were analyzed for a diverse suite of contaminants, including several metals, POP, and PAH. The general categories of contaminants can be found in Table 2 and Table 3, with data for each contaminant analyzed available in a comprehensive electronic table accompanying this



report. Metals were analyzed by Katie Downey at TestAmerica Lab (Tacoma, WA) in 2007 and 2009, and by Teri Torres at the same lab in 2011. PAH analyses were conducted by Marie Larsen at NOAA Ted Stevens Marine Research Institute Auke Bay Lab (Juneau, AK). POP analyses were conducted by Gina Ylitalo at NOAA Montlake Lab (Seattle, WA). Each of the three labs that conducted the analyses provided details of the lab protocols used. These protocols are either included in this document or, if extremely detailed, can be found in accompanying citations and electronic documents that accompany this report.

Because contamination levels are generally very low throughout SEAN parks, analytes are reported primarily by general category, rather than individual analyte. However, electronic files submitted to NPS with this report contain individual results for all analytes and can be easily accessed.

### **Metals Analyses**

Mussel samples were analyzed by TestAmerica to quantify arsenic (As), cadmium (Cd), mercury (Hg), and tributyltin (TBT) levels. Only a few samples were analyzed for TBT levels because they are very expensive to quantify. Detailed lab protocols for the metals analyses were provided by TestAmerica and are included in accompanying electronic documents. Sediment samples were not analyzed for metal contamination.

### **PAH Analyses**

PAH analyses of mussel and sediment samples were conducted at Auke Bay Laboratory by Marie Larsen following protocols developed there and described in a 80-page electronic document that accompanies the final report submitted to SEAN parks (Larsen et al. 2008). TPAH values are presented here, but more detailed data on the individual PAH compounds that contribute to the total value can be found in the electronic data files provided to NPS with this report.

### **POP Analyses**

All mussel POP included in this project were analyzed by Gina Ylitalo at NOAA Montlake Lab (Seattle, WA). Prior to analysis, the blue mussels were removed from their shells. The mussel composite samples were homogenized, extracted, and analyzed for POPs using the method of Sloan et al. (2005). This method involves: (1) extraction of tissue using methylene chloride in an accelerated solvent extraction procedure, (2) clean-up of the methylene chloride extract on a single stacked silica gel/alumina column, (3) separation of POP from the bulk lipid and other biogenic material by high-performance size exclusion liquid chromatography, and (4) analysis on a low resolution quadrupole GC/MS system equipped with a 60-meter DB-5 GC capillary column. The instrument was calibrated using sets of up to ten multi-level calibration standards of known concentrations. Following this procedure, a total of 40 PCB and 10 PBDE congeners and 24 chlorinated pesticides were determined in these samples. Total lipid in the blue mussel samples was measured by a thin-layer chromatography flame ionization method (Ylitalo et al. 2005).

All contaminant concentrations in this document are reported in ng/g wet weight or ppb.  $\Sigma$ PCB is the sum of 40 congeners, including: 17, 18, 28, 31, 33, 44, 49, 52, 66, 70, 74, 82, 87, 95, 99, 101/90, 105, 110, 118, 128, 138/163/164, 149, 151, 153/132, 156, 158, 170, 171, 177, 180, 183, 187/159/182, 191, 194, 195, 199, 205, 206, 208, and 209.  $\Sigma$ DDT is the sum of *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT and *p,p'*-DDT.  $\Sigma$ CHLD is the sum of oxychlordane, *gamma*-chlordane, nona-III-chlordane, *alpha*-chlordane, *trans*-nonachlor and *cis*-nonachlor.

$\Sigma$ HCH is the sum of *alpha*-, *beta*-, and *gamma*-HCH isomers, and  $\Sigma$ PBDE is the sum of congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, 183.

As part of performance-based laboratory quality assurance (Sloan et al. 2006), quality control samples [a method blank, replicate and Standard Reference Materials (SRMs, e.g., NIST 1974b and 1947)] were analyzed with each sample set. Results obtained for SRMs 1974b and 1947 were in excellent agreement with certified and reference values published for these materials by the National Institute of Standards and Technology. In addition, the other quality control samples met established laboratory criteria. Sediment samples were analyzed for PAH, but not metals or POP. Sum POP values are presented, but more detailed data on the individual congeners that contribute to the total value can be found in the electronic data files provided to NPS with this report.

## Results and Discussion

A total of 71 mussel and sediment samples were collected from throughout SEAN parks and surrounding areas in 2007, 2009, and 2011 (Table 1). From these samples, it is evident that SEAN parks have low levels of intertidal contamination across the suite of metal, PAH, and POP contaminants analyzed. Furthermore, SEAN parks and the surrounding areas appear to be relatively pristine compared to most of the US (Kimbrough et al. 2008). Those few sites inside or outside of SEAN park boundaries non-randomly selected for sampling as hot controls because of their heavy human use, generally show higher levels of TPAH and POP than sites selected at random within SEAN parks. Patterns in the metal contaminants analyzed suggest SEAN parks have relatively low levels of contamination and what little contamination exists is primarily from localized sources, rather than regional or global inputs.

Comparisons among sites throughout the SEAN park region reveal that the most contaminated sites are outside KLGO and SITK park boundaries in areas of heavy human use. This is perhaps not too surprising given the close proximity of SITK and KLGO to urban centers and heavy boat traffic. Although there is evidence of different types of contaminants reaching relatively high levels at several different sites in and nearby SEAN parks, the overall contamination levels are low. Each of the major categories of contaminants is described separately in greater detail below.

### Metals

Metal contamination levels are low throughout GLBA. There are some sites in which specific metals reach relatively high levels for the SEAN region, but all of these are still on the low end of the range of values obtained from mussels in the contiguous US. Arsenic and Cadmium levels are < 2 ppm (ug/g) throughout SEAN parks, and are very low relative to values obtained from the MWP in other parts of Alaska and the contiguous 48 states (Kimbrough et al. 2008). There is little evidence either of these contaminants has a consistent geographic pattern or reaches high levels in areas chosen as hot controls. Similarly, mercury levels are low throughout SEAN parks (< 0.03 ppm). However, the highest mercury levels were found in two mussel sample from a hot control site in Crescent Harbor (1801707 & 201106), outside the boundaries of SITK. TBT is present at a detectable level (52.46 ppb) only in the 2007 from at this site, as well. Overall, the values for these metals are low relative to those found in the most recently published MWP report, which outlines 20 years of data compiled for mussels collected in both Alaska and the rest of the US (Kimbrough et al. 2008). The few sites sampled in 2007, 2009, and 2011 show consistent patterns of low metals contamination, though values are generally a bit lower in 2009 than 2007.

This suggests that much of southeast Alaska and SEAN parks, in particular, are relatively unimpacted by metal contaminants in the intertidal zone.

**Table 2.** Metal contaminant levels in mussel samples collected from SEAN parks and nearby areas. All concentrations reported as ug/g wet tissue except TBT, which are reported as ng/g.

Sample	Park	Site Description	As	Cd	Hg	TBT
1801601	KLGO	Dyea	0.69	0.56	0.0070	<LOQ
1801602	KLGO	Skagway Harbor*	0.58	0.61	0.0140	<LOQ
1801606	GLBA	Barlett Cove	0.71	0.52	0.0093	<LOQ
1801607	GLBA	Barlett Cove	0.60	0.41	0.0088	<LOQ
1801608	GLBA	B Boat Ramp*	0.88	0.49	0.0082	<LOQ
1801609	GLBA	Ripple Cove	0.70	0.51	0.0086	NA
1801610	GLBA	N Rush Point	0.67	0.63	0.0091	NA
1801611	GLBA	S Whidbey Psg	0.83	0.82	0.0071	NA
1801612	GLBA	N Drake Island	0.77	0.90	0.0063	<LOQ
1801613	GLBA	Geikie Inlet Isl	0.46	0.40	0.0079	NA
1801614	GLBA	Sebree Island	0.77	0.75	0.0057	NA
1801615	GLBA	N Caroline Pt	0.89	0.90	0.0067	<LOQ
1801616	GLBA	Muir Pt	0.63	0.51	0.0058	NA
1801617	GLBA	N Pt George	0.73	0.74	0.0073	NA
1801618	GLBA	Gateway Knob	0.68	0.55	0.0066	<LOQ
1801619	GLBA	Hunters Cove	0.53	0.51	0.0065	NA
1801620	GLBA	Spokane Cove	0.55	0.69	0.0065	NA
1801621	GLBA	B Fuel Dock*	0.51	0.41	0.0094	<LOQ
1801622	GLBA	Bartlett R Trib	0.96	0.37	0.0110	NA
1801623	GLBA	S. Stump Cove	1.10	0.75	0.0065	NA
1801624	GLBA	Westdahl Pt	0.60	0.51	0.0057	NA
1801625	GLBA	N Nunatak Cr	1.00	0.76	0.0074	NA
1801626	GLBA	McBride Spit South	1.00	0.68	0.0074	NA
1801628	GLBA	Tidal inlet	0.91	1.20	0.0065	<LOQ
1801629	GLBA	E Russell Rocks	0.71	0.60	0.0051	NA
1801630	GLBA	Russell Fan	0.77	0.53	0.0057	NA
1801631	GLBA	Russell Island	1.00	0.58	0.0070	<LOQ
1801632	GLBA	N of Russell Fan	0.71	0.41	0.0071	NA
1801633	GLBA	S Tarr Inlet	1.10	0.49	0.0053	NA
1801634	GLBA	Tarr Inlet	1.00	0.47	0.0076	<LOQ
1801635	GLBA	W Hazelton Camp	1.80	0.76	0.0069	NA
1801636	GLBA	Blue Mouse Cove	0.56	0.37	0.0075	NA
1801638	GLBA	Upper Excursion	0.55	0.44	0.0083	NA
1801640	GLBA	Excursion Fish Plt*	0.47	0.60	0.0086	<LOQ
1801641	GLBA	Lower Excursion	0.50	0.84	0.0046	NA
1801642	GLBA	NE Pleasant Island	0.57	0.40	0.0046	NA
1801643	GLBA	E Carolus R	0.63	0.50	0.0081	NA
1801645	GLBA	W Carolus	0.6	0.73	0.0067	<LOQ
1801646	GLBA	W Pt Dundas	0.49	0.53	0.0067	NA
1801648	GLBA	W Dundas Bay	0.49	0.30	0.0068	NA
1801649	GLBA	Outer Elfin Cove*	0.75	0.47	0.0100	<LOQ
1801650	GLBA	Mouth Rush Pt Cr	0.56	0.61	0.0071	NA
1801701	GLBA	Graves	1.10	0.90	0.0097	NA
1801702	GLBA	Torch Bay N	0.71	1.00	0.0100	<LOQ
1801703	GLBA	Dixon Harbor	0.80	0.73	0.0110	NA

Table 2. (continued) Metal contaminant levels in mussel samples collected from SEAN parks and nearby areas. All concentrations reported as ug/g wet tissue except TBT, which are reported as ng/g.

Sample	Park	Site Description	As	Cd	Hg	TBT
1801704	GLBA	Lituya Bay	0.52	0.39	0.0057	NA
1801705	SITK	Visitor's Center	0.75	0.63	0.0073	<LOQ
1801706	SITK	Indian R	0.79	0.70	0.0068	<LOQ
1801707	SITK	Crescent Harbor*	1.00	0.33	0.0210	52.46
1801708	GLBA	Berg Bay	0.51	0.37	0.0075	<LOQ
200901	GLBA	E Russell Rocks	0.26	0.15	0.0025	<LOQ
200902	GLBA	W Hazelton Camp	0.52	0.18	0.0022	<LOQ
200903	GLBA	Ripple Cove	0.53	0.26	0.0023	<LOQ
200904	GLBA	Bartlett Cove	1.10	0.75	0.0084	<LOQ
200905	SITK	Visitor's Center	0.53	0.13	0.0068	<LOQ
200906	SITK	Crescent Harbor*	0.39	0.14	0.0031	<LOQ
201101	GLBA	E Russell Rocks	1.80	1.00	0.0170	<LOQ
201102	GLBA	W Hazelton Camp	1.30	1.20	0.0120	<LOQ
201103	GLBA	Ripple Cove	1.40	1.30	< LOQ	<LOQ
201104	GLBA	Bartlett Cove	1.10	1.30	0.0100	<LOQ
201105	SITK	Visitor's Center	0.95	0.25	0.0140	<LOQ
201106	SITK	Crescent Harbor*	1.10	0.86	0.0260	<LOQ

\*indicates site selected as hot control as described in text.

<LOQ = below quantitation limits

NA = not analyzed due to high expense of analysis

## PAH

The SEAN parks region shows low levels of TPAH contamination, though TPAH was detected at low levels in a number of sites (Table 3). Five samples have TPAH concentrations above 100 ppb (=ng/g), five samples have TPAH concentrations within the range of 10-70 ppb, and all other samples are below 10 ppb.

Most of the samples with detectable TPAH levels were collected from hot control sites. These sites appear to be impacted by either creosote or petrochemicals associated with internal combustion engines. The highest TPAH contamination detected is in a mussel sample taken from the Bartlett fuel dock (1801621) in GLBA, which has a concentration of 1488 ppb. This is the only site and contaminant samples in 2007 from within SEAN park boundaries that ranks as a "medium" level of contamination relative to the rest of the US (Kimbrough et al. 2008). Closer inspection of the relative PAH profiles from this sample indicates the origin of this contamination is most likely creosote. This is consistent with the construction materials used to build the old dock at this site. In contrast, the high TPAH (406.01 ppb) found in sediment near the SITK Visitor Center (1801709) in 2007 is most consistent with a weathered petrogenic source.

The two samples analyzed from KLGO in 2007 also have detectable TPAH levels, which is consistent with high boat use in that area and its location at north end of Lynn Canal. However, these TPAH values are low relative to the rest of the US. The high TPAH found in mussels in

Crescent Harbor near SITK in 2009 and 2011 are consistent with the heavy boat use in this area both historically and presently.

The most surprising PAH result is a 2007 mussel sample from Berg Bay (1801708), GLBA, which has 138 ppb of TPAH, and a profile of constituent compounds which suggests a recent petrogenic source. This level of TPAH may result from a combination of boat use of this bay prior to sampling and the low rate of seawater exchange of this bay with the rest of lower GLBA due to a shallow entrance to Berg Bay. It is also worth mentioning that TPAH were detectable in all four GLBA sites sampled in 2009 and 2011, but at such low levels (~1 ppb or less) that they do not indicate any level of contamination that would be cause for concern.

Results from this and other studies focused on a variety of different organisms in Alaska imply that most PAH impacts in Alaska are primarily of local origin with little input from more distant sources (Moles et al. 2006, Landers et al. 2008). Recent studies of a variety of plants and fishes inhabiting this and other parts of the US generally support the assertion that PAH contamination in SEAN park mussels is very low (Landers et al. 2008, Olson et al. 2008).

## POP

The SEAN region also shows very low levels of contamination in the major POP groups analyzed. In most cases POP detections occurred at hot controls or were very near lower detection limits (Table 3). All samples analyzed, except one near the Excursion Inlet fish plant and the 2009 and 2011 Crescent Harbor samples, have  $\Sigma$ CHLD levels < LOQ. Only eleven samples from seven sites have detectable  $\Sigma$ DDT levels, and all of these are still far below 5 ppb. In addition, all of these sites are heavy human use areas in or near KLGO, SITK, and GLBA. Endosulfan and lindane, which are present-use pesticides, are at concentrations of < 1 ppb in all samples (data not shown). A few sites have  $\Sigma$ HCH levels that are above detection limits. However, these values are very low (< 1 ppb), providing little evidence HCH contamination is a problem in the intertidal zone of SEAN parks. The six 2011 samples show a slight increase in  $\Sigma$ HCH levels, but the values are just above the detection limits, so the observed values are unlikely to indicate any strong temporal trend in HCH.

$\Sigma$ PCB levels are above detection limits in many samples, but are still extremely low in all but a few samples. In most cases, the values hover near the lower detection limits. The sites with relatively high  $\Sigma$ PCB levels for the SEAN region have heavy human use. The seven samples with the highest values are from the SITK area. Nevertheless, most of the sites with the highest levels of  $\Sigma$ PCB in the SEAN would be categorized as low relative to the most recent data from mussel samples across the US (Kimbrough et al. 2008).

All of the sites included in this study had  $\Sigma$ PBDE levels < 10 ppb. Most of the sites with detectable  $\Sigma$ PBDE levels are ones selected as hot controls. However,  $\Sigma$ PBDE were detected at very low levels (< 1 ppb) in 2011 samples from East Russell Rocks (201101) and Bartlett Cove (201102), where they had not been detected in 2007 or 2009. Still, these values are just above detection limits. The fact that six sites sampled in 2007, 2009, and 2011, show similar levels of POP contamination over time suggests that the patterns we observed in the more extensive survey 2007 are fairly stable and representative of baseline conditions. There appears to be very little  $\Sigma$ PBDE contamination in SEAN, except at a few hot control sites.

**Table 3.** TPAH and POP contamination levels (ng/g) in sediment and mussel samples from SEAN parks and nearby areas.

Sample	Park	Site Description	TPAH	$\Sigma$ CHLD	$\Sigma$ DDT	$\Sigma$ HCH	$\Sigma$ PCB	$\Sigma$ PBDE
1801601	KLGO	Dyea	2.69	< LOQ	0.11	< LOQ	1.6	< LOQ
1801602	KLGO	Skagway Harbor*	42.82	< LOQ	0.22	< LOQ	2.1	0.42
1801603	GLBA	Berg Bay	NA	< LOQ	< LOQ	< LOQ	1	< LOQ
1801604	GLBA	Berg Bay	NA	< LOQ	< LOQ	< LOQ	1.3	< LOQ
1801605	GLBA	Berg Bay	NA	< LOQ	< LOQ	< LOQ	1.3	< LOQ
1801606	GLBA	Barlett Cove	< LOQ	< LOQ	< LOQ	< LOQ	1.4	< LOQ
1801607	GLBA	Barlett Cove	< LOQ	< LOQ	< LOQ	< LOQ	0.62	< LOQ
1801608	GLBA	B Boat Ramp*	< LOQ	< LOQ	< LOQ	< LOQ	1.2	< LOQ
1801609	GLBA	Ripple Cove	< LOQ	< LOQ	< LOQ	< LOQ	0.77	< LOQ
1801610	GLBA	N Rush Point	< LOQ	< LOQ	< LOQ	< LOQ	0.69	< LOQ
1801611	GLBA	S Whidbey Psg	< LOQ	< LOQ	< LOQ	< LOQ	0.79	< LOQ
1801612	GLBA	N Drake Island	< LOQ	< LOQ	< LOQ	< LOQ	0.64	< LOQ
1801613	GLBA	Geikie Inlet Isl	< LOQ	< LOQ	< LOQ	< LOQ	0.65	< LOQ
1801614	GLBA	Sebree Island	< LOQ	< LOQ	< LOQ	< LOQ	0.7	< LOQ
1801615	GLBA	N Caroline Pt	< LOQ	< LOQ	< LOQ	< LOQ	0.14	< LOQ
1801616	GLBA	Muir Pt	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
1801617	GLBA	N Pt George	< LOQ	< LOQ	< LOQ	< LOQ	0.72	< LOQ
1801618	GLBA	Gateway Knob	< LOQ	< LOQ	< LOQ	< LOQ	0.78	< LOQ
1801619	GLBA	Hunters Cove	< LOQ	< LOQ	< LOQ	< LOQ	0.65	< LOQ
1801620	GLBA	Spokane Cove	NA	< LOQ	< LOQ	< LOQ	0.67	< LOQ
1801621	GLBA	B Fuel Dock*	1488.27	< LOQ	< LOQ	< LOQ	2.2	< LOQ
1801622	GLBA	Bartlett R Trib	< LOQ	< LOQ	< LOQ	< LOQ	1	< LOQ
1801623	GLBA	S Stump Cove	< LOQ	< LOQ	< LOQ	< LOQ	1.7	< LOQ
1801624	GLBA	Westdahl Pt	< LOQ	< LOQ	< LOQ	< LOQ	1.5	< LOQ
1801625	GLBA	N Nunatak Cr	< LOQ	< LOQ	< LOQ	< LOQ	1.1	< LOQ
1801626	GLBA	McBride Spit S	< LOQ	< LOQ	< LOQ	< LOQ	0.72	< LOQ
1801627	GLBA	McBride Spit S	< LOQ	NA	NA	NA	NA	NA
1801628	GLBA	Tidal inlet	< LOQ	< LOQ	< LOQ	0.18	0.87	< LOQ
1801629	GLBA	E Russell Rocks	< LOQ	< LOQ	< LOQ	< LOQ	1.2	< LOQ
1801630	GLBA	Russell Fan	< LOQ	< LOQ	< LOQ	< LOQ	0.78	< LOQ
1801631	GLBA	Russell Island	< LOQ	< LOQ	< LOQ	< LOQ	1	< LOQ
1801632	GLBA	N Russell Fan	< LOQ	< LOQ	< LOQ	0.21	1.2	< LOQ
1801633	GLBA	S Tarr Inlet	< LOQ	NA	NA	NA	NA	NA
1801634	GLBA	Tarr Inlet	< LOQ	< LOQ	< LOQ	< LOQ	0.66	< LOQ
1801635	GLBA	W Hazelton Camp	< LOQ	< LOQ	< LOQ	< LOQ	0.66	< LOQ
1801636	GLBA	Blue Mouse Cove	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
1801637	GLBA	Blue Mouse Cove	3.59	NA	NA	NA	NA	NA
1801638	GLBA	Upper Excursion	< LOQ	< LOQ	< LOQ	< LOQ	0.54	< LOQ
1801639	GLBA	Upper Excursion	6.94	NA	NA	NA	NA	NA
1801640	GLBA	Excursion Fish Plt*	13.55	0.45	0.25	< LOQ	1.8	< LOQ
1801641	GLBA	Lower Excursion	< LOQ	< LOQ	< LOQ	< LOQ	0.79	< LOQ
1801642	GLBA	NE Pleasant Island	< LOQ	< LOQ	< LOQ	< LOQ	1.2	< LOQ
1801643	GLBA	E Carolus R	< LOQ	< LOQ	< LOQ	< LOQ	1	< LOQ
1801644	GLBA	E Carolus R	< LOQ	NA	NA	NA	NA	NA
1801645	GLBA	W Carolus	< LOQ	< LOQ	< LOQ	< LOQ	1.1	< LOQ
1801646	GLBA	W Pt Dundas	< LOQ	< LOQ	< LOQ	< LOQ	1.1	< LOQ

Table 3. (continued) TPAH and POP contamination levels (ng/g) in sediment and mussel samples from SEAN parks and nearby areas.

Sample	Park	Site Description	TPAH	ΣCHLD	ΣDDT	ΣHCH	ΣPCB	ΣPBDE
1801647	GLBA	W Pt Dundas	<LOQ	NA	NA	NA	NA	NA
1801648	GLBA	W Arm Dundas	<LOQ	< LOQ	< LOQ	< LOQ	1.2	< LOQ
1801649	GLBA	Outer Elfin Cove*	69.74	< LOQ	0.48	< LOQ	3.7	6.3
1801650	GLBA	Mouth Rush Pt Cr	<LOQ	< LOQ	< LOQ	< LOQ	0.77	< LOQ
1801701	GLBA	Graves	<LOQ	< LOQ	< LOQ	< LOQ	0.65	< LOQ
1801702	GLBA	Torch Bay N	<LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
1801703	GLBA	Dixon Harbor	<LOQ	< LOQ	< LOQ	< LOQ	0.84	< LOQ
1801704	GLBA	Lituya Bay	NA	< LOQ	< LOQ	< LOQ	1.1	< LOQ
1801705	SITK	Visitor's Center	2.70	< LOQ	0.75	< LOQ	7.1	< LOQ
1801706	SITK	Indian R	<LOQ	< LOQ	0.4	< LOQ	5.1	< LOQ
1801707	SITK	Crescent Harbor*	<LOQ	< LOQ	1.3	< LOQ	15	3.2
1801708	GLBA	Berg Bay	137.66	NA	NA	NA	NA	NA
1801709	SITK	Visitor's Center	406.01	NA	NA	NA	NA	NA
200901	GLBA	E Russell Rocks	0.83	< LOQ	< LOQ	< LOQ	0.36	< LOQ
200902	GLBA	W Hazelton Camp	1.09	< LOQ	< LOQ	< LOQ	0.33	< LOQ
200903	GLBA	Ripple Cove	0.48	< LOQ	< LOQ	< LOQ	0.35	< LOQ
200904	GLBA	Bartlett Cove	0.78	< LOQ	< LOQ	< LOQ	0.36	< LOQ
200905	SITK	Visitor's Center	12.73	< LOQ	0.22	< LOQ	4.1	< LOQ
200906	SITK	Crescent Harbor*	949.22	0.20	0.95	1.5	14	3.5
201101	GLBA	E Russell Rocks	0.34	< LOQ	< LOQ	0.32	< LOQ	0.16
201102	GLBA	W Hazelton Camp	0.30	< LOQ	< LOQ	0.33	0.32	< LOQ
201103	GLBA	Ripple Cove	0.84	< LOQ	< LOQ	0.41	< LOQ	< LOQ
201104	GLBA	Bartlett Cove	0.67	< LOQ	< LOQ	0.29	< LOQ	0.50
201105	SITK	Visitor's Center	17.28	< LOQ	1.1	0.57	4.0	0.96
201106	SITK	Crescent Harbor*	514.87	0.17	4.7	< LOQ	7.8	3.8

\*indicates site selected as hot control as described in text.

<LOQ = below quantitation limits

NA = not analyzed (in most cases because POP analyses were restricted to mussel samples)

The POPs levels found in SEAN park mussels and sediment are low relative to values obtained from other parts of the US and well below most standards for seafood. The National Academy of Sciences set limits for seafood for PCB, DDT, and CHLD of 2,000 ppb, 5,000 ppb, and 300 ppb, respectively (Sciences 1991). Mussels and sediment sampled in the present study have values orders of magnitude below these levels. Recently, Heintz (2006) reported 5.00 ppb of 15 congeners of PCBs, 4.93 ppb of five DDT, and 1.15 ppb HCB, in walleye pollock from SEAK. The values we detected are all below these DDT and HCB values, with only a few sites from the SITK area showing PCB levels higher than these pollock. POP levels in SEAN park mussels are generally well below values obtained in the rest of the US (Kimbrough et al. 2008). POP levels in SEAN park mussels are also well below salmon and sculpin contaminant levels in heavily impacted Commencement Bay, WA (Olson et al. 2008). A recent report showed that GLBA has very high levels of HCH and HCB in conifer needles relative to other national parks included in a broad study of national parks (Landers et al. 2008), but we detected only low levels (< 1 ppb) in intertidal mussels and sediments this study. This could be due to a general pattern seen in



many studies in which many POPs accumulate at higher concentrations at higher elevations due to “cold fractionation” (Landers et al. 2008), or due to different transport mechanisms of these contaminants through marine versus terrestrial ecosystems. The POP levels obtained in this study are very similar to values obtained from a concurrent study of coho salmon in GLBA and SITK (S. Nagorski, UAS, unpubl. data), lending weight to the results presented here.

## Conclusions

The most important result of this extensive study of mussel and sediment samples from sites in and around SEAN parks is that this region has low levels of intertidal contamination. These data provide a useful baseline for a variety of potential contaminants in southeast Alaska and suggest this region is relatively pristine. For nearly every contaminant considered here, values obtained from sites throughout SEAN parks are well below values found in samples from other US states as a part of the MWP, which serves as a valuable baseline for comparison to SEAN. The TBT, POP, and PAH levels were too low to be detectable in many of the samples, and in many others the levels were just above the lower detection limits. Sites chosen as hot controls because of relatively heavy human activity in and around GLBA, SITK, and KLGO, have high levels of some contaminants relative to the rest of SEAN parks. However, both mussel and sediment samples suggest the levels of contamination are almost uniformly well below values considered health threats to humans.

The general patterns of the highest contaminant levels being present in non-randomly selected, hot control sites, as well as a lack of any large-scale contamination across multiple sites, imply that most contamination is from local sources rather than from high rates of regional atmospheric deposition or other large scale mechanisms. KLGO and SITK show relatively high levels of contamination because they are located in or near areas of high human density where point sources of contamination are found. However, there are small hotspots of specific contaminants in or near each park. For example, the Bartlett Cove fuel dock in GLBA has TPAH levels that are an order of magnitude higher than most other sites. Crescent Harbor near SITK has the highest TBT, mercury,  $\Sigma$ DDT, and  $\Sigma$ PCB levels in the 2007, 2009, and 2011 samples. This pattern of the highest levels of contamination being associated with areas of the highest human use and density is consistent with previous findings for other parts of Alaska and the US (Frenzel 2000, Kimbrough et al. 2008).

Although there is little evidence of large scale contamination in SEAN parks, there is reason to remain vigilant. PAH are unlikely to be a regional concern in the near future, because the most likely short-term threats to SEAN parks are catastrophic events from local PAH sources and heavy boat traffic (Eckert et al. 2006b, a, Hood et al. 2006). In fact, during this study a small cruise ship ran aground in GLBA, but fortunately did not produce a large PAH spill. Even without a catastrophic event, PAH from marine vessels seems the most likely contamination threat to the intertidal of SEAN parks. Another reason to continue to monitor contaminants in SEAN parks is that very low levels of some contaminants from distant sources can cause biologically damaging impacts in the form of developmental or reproductive problems, as recent studies have shown (Hayes et al. 2003, Hu et al. 2009).

Although a variety of threats could impact the Gulf of Alaska, including southeast Alaska (MacDonald et al. 2003), the results obtained here are reassuring. When compared to the contaminants data obtained from over 20 years as a part of the MWP, SEAN parks are relatively pristine and would seem likely to remain so into the near future, as long as catastrophic events can be avoided.

## Recommendations

There is no evidence from this study that current contamination levels pose any widespread, detectable threat to the intertidal zone of SEAN parks. However, the low levels of contaminants and their spatial distributions suggest that it would be worthwhile to continue monitoring relatively pristine and hot control sites throughout SEAN parks at low levels of sampling effort. In addition, the largely uncertain and sometimes counterintuitive relationships between contaminant dosages and biological impacts argue for continued vigilance and monitoring. More specifically, it seems wise to obtain mussel samples from sites within and nearby each SEAN park every two to five years. It would also be wise to repeat the broad scale sampling conducting in 2007 at a decadal interval. This level of effort would provide insight into any potential increases in contamination and also provide a means to monitor the most likely point sources of contaminants near the SEAN park boundaries, as well as indications of any large scale trends in contaminants. It would also be wise to continue using the MWP sampling protocol and to use the vast MWP dataset to contextualize SEAN park contaminant levels, because the MWP provides the most rigorous, extensive, and longest continuous contaminants dataset in the US. These steps will make it easier for the NPS to detect contaminants and to make valid and useful inferences with their future sampling efforts. SEAN will be pursuing a formal, long-term partnership with the MWP in 2013.



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# Appendix A

## Collection, Preservation and Shipping Instructions Mussel Watch Samples

### COLLECTION DATE

To ensure compatibility with the historic Mussel Watch Project data, sampling will occur between mid-November and the end of March. The criterion for the annual sampling of a MWP site requires that samples be collected within three weeks of the date the site was first sampled. The intention of sampling all sites in this time frame is to avoid the possible effects of spawning on chemical concentrations. Bivalves are collected within the same six week window biennially (three weeks before and after target sampling date). Sampling dates vary by region and site; for dates relevant to each region or site consult NOAA Technical Memorandum NOS ORCA 112. Sampling should occur at a time of the tidal cycle that makes sampling possible.

### ACCESSING THE SITE

Select a day/time for collection convenient to you and meeting the target and tide criteria. Date must be in a six week window, within 3 weeks of the target collection date (NOAA Technical Memorandum NOS ORCA 112). Time must correspond to a tidal stage or lower at which the mussels are easily accessible.

If you plan to collect at a time coinciding with low tide (check a tide table), there will be no problem with access. Height of collection (above the water level at the time of collection) and height of the highest mussel distribution is information to be recorded at the time of collection.

### SAMPLE COLLECTION

At each site approximately 60 mussels are collected for contaminant analyses (trace elements and organics) and another 20 for histopathology. If the specimens are smaller than half an inch, collect more for contaminant analyses (up to about 160). Enough sample is needed for both sufficient biomass as well as numbers for statistical significance. Thus, if samples are small more are needed to get the biomass. Regardless of specimen size, a minimum of 60 individuals are needed. For histopathology analyses specimen size makes no difference, but numbers are important, 20 is the minimum.

Samples for chemistry and histopathology can be co-mingled until time of shipping. There is no need to separate them in the field and care and handling is the same (see precautions below).

Site descriptions sometimes differentiate collection at 3 distinct "stations". Frequently when new sites are established 3 unique stations are collected within a site. For intertidal sites this would be three locations along 100 M of shoreline. For subtidal sites this would be three dredge transects in a 400 M (radius) area. Even for repeat sites if possible distribute the collection among these stations, with the samples packaged separately. Samples will be composited in the laboratory but retaining individual sample identity allows more extensive laboratory analyses to occur if

unusual sample contaminant concentrations are found. At all sites it is not possible or practical to delimit three separate stations at each site. In such a case, make the collection without distinction, but separate the "picking" as best you can spatially. The purpose of this is to avoid sampling a single "clump" of mussels.

### Observations

Measure water temperature at the site and collect the small vial of seawater for salinity determination. Document collection information (site, date, time, temp, check that salinity has been collected, and any relevant comments). Determine the center of the sampling location using GPS.

Note any circumstances that might influence contaminant levels, future collection, or health of the mussels. Typical observations might include

- Notices of shellfish closures or prohibitions on fishing posted near the site
- Oil sheen on water, weathered oil on rocks, unusual odors
- Known discharges or releases in the area (outfalls nearby, recent oil spills, recent runoff from heavy rain, etc.)
- Depauperate or declining populations
- Limitations to accessibility

Two heights (relative to the water level at the time of collection) should be noted. Simply estimate these heights. Height of collection refers to the height above the water level at the time of collection. For example if samples are collected three feet above the water level sample height is indicated as 3 or if samples are collected at water level, the height of collection is 0. The other value is height of highest access. For example, mussels are at current water level, but you note that mussels are available up the intertidal zone (the vertical extent which is washed by the tides) all the way up to approximately 6 feet above the current water level, then the Highest Access is 6 feet. On the other hand if you collect at water level (0 feet) and find that these are the only mussels, the Height of Highest Access in this instance is also 0 feet. By correlation with time of collection and a graphical depiction of the tide we can calculate the tide stage (and hence time for future collections) when we expect mussels to become accessible.

Place the waterproof paper card in one of the bags that will be sent to the contract laboratory.

### Salinity and temperature

At the site, fill the small plastic vial with seawater which is used to measure salinity. Tape the lid securely. Place the vial in the ice chest with the mussels. Measure the sea water temperature at the time of collection. A regular outdoor thermometer placed in the water or in a bucket of water will do.

## Holding, packing and shipping

The ideal scenario would be to collect the samples in the early afternoon, pack them for shipping and deliver them (or have them picked up by) to an overnight courier by the cut off time (same day as collection) for next day delivery. However, this is not always possible for all tidal scenarios and sample locations.

## Transport process

Keep the transit time (collection until delivery to the labs) to a minimum, especially the time the samples are with the courier. It is preferable that samples be held by the field team rather than by the courier. For example, if samples are collected on a Saturday, keep samples until Monday and monitor their holding condition rather than dropping them off at courier location on Saturday for a Monday delivery. Similarly, do not leave samples with a courier after the last scheduled shipment for that day. Keep the samples until the next day.

Keep the samples cold on ice but not frozen in a ziploc bag, and well drained (no standing water, either fresh or seawater). Ice should be package in separate bags and is discussed below.

## Prior to shipping

Keep samples on ice (in a ziploc bag) until ready for shipping. Note, contact with water will invariably cause the mussels to open. Opening will introduce the possibility for contamination or depuration, and if the water is fresh it will kill the mussels, rendering them useless for the study. The preferred method is to place the mussels in a ziploc bag and place this on top or beneath another ziploc bag filled with ice. It is also OK to store the mussels in a refrigerator if an extended hold (overnight) is required. Note all bags into which mussels are placed should have the appropriate site and date marked with a waterproof pen.

1. Don't put ice in the bags with the specimens.
2. Don't allow them to freeze (this is a caution peculiar to the Alaska and few east coast sites almost exclusively, in winter).

Mussels can be held then for days on ice in this way if the sample bags are not sealed and are kept free of fresh water. Periodically examine the bags of mussels to ensure that any entrained water has not leaked into the mussels' container. If standing water is observed, drain it from the mussels.

## Packaging

When it comes time to ship the samples divide the number of mussels for contaminant analyses (60 to 160) into two ziploc bags destined for one (larger) ice chest and the histopathology mussels (20 regardless of size) in another ziploc bag and into a smaller ice chest. Mussels for contaminant and histopathology analyses can all be chilled and held together. Put ice into separate ziploc bags, not into the chest directly. Drained mussels are placed in their own bag(s), ice is in its own bag(s). Thus, water is contained as it melts and the mussels are segregated from any leaks or contamination by their sample bags.

If the samples are chilled well before shipping (overnight or days) it will not require a lot of ice to keep them cold as they will have stored a lot of cold already but it better or err on the side of caution and add extra ice. Bagged ice is placed beneath the samples, and bagged ice added on top of the samples. Samples should be packaged and iced in such a way that the specimens will not be compromised if there is a day or two delay in transit.

### Shipping

The best method is to take the ice chests to an overnight courier office or authorized agent. Another acceptable method is to call the courier company the morning or day before sampling and arrange for a Pick Up by their driver. Do not leave the ice chest unattended at a drop box or a location which is not an authorized agent.

1. One ice chest (with 20 mussels in a single ziploc bag) goes to the laboratory performing the gonadal index and histopathology analyses.
2. The other ice chest containing two ziploc bags of mussels (with approximately 30 large or 80 small mussels each), the data card, and the vial of seawater goes to contracting laboratory performing the organic contaminant or trace element analyses.

### Sealing and labeling

Use at least 3 separate bands of multiple wraps of fiber tape to close the container. Put the data sheet in a ziploc bag and send it back with the samples. Keep a copy of the collection information for yourself. Put three or four address labels on the respective ice chests in addition to the airbill. Cover these address labels with wide clear tape.

Packaging and Labeling is illustrated in the figures that follow.

### **Packaging NS&T Samples for Shipment**

1. Bagged ice on bottom.



2-Drained, bagged samples with label laid on ice. Site label and salinity vial with samples.



3. Bagged samples layered between bags of ice.



4- Bagged ice on top. Fill void with more ice.



5. Three address labels



6- Sealed with at least two bands of (3 wraps each) fiber tape, and 1 band wide clear tape wide clear tape. Airbill and tag affixed to chest with fiber tape, not handle.



## **PRECAUTIONS**

1. The samples must arrive for histopathology and gonadal index determinations alive. If there is a substantial unavoidable delay of several days between collection and shipping of samples, the contaminant mussels can be frozen solid and held in that condition for quite some time if they are not allowed to thaw. In this case samples must be kept frozen solid when shipped which requires the use of dry ice. Such a delay and sample treatment will invalidate the histopathology and gonadal index samples.
2. None of the samples should be allowed to freeze (with the exception above) or to warm up.
3. Keep specimens out of water (don't let them stand in salt water or in ice water melt). This will cause them to open up and introduce possible contamination or specimen death.
4. The samples will be analyzed for trace metal and organic contaminants. Avoid situations where these can be introduced (oil, fuel, pesticide, PCBs, exhaust fumes, flaking or rusty metal).
5. Avoid collection of samples on other than natural substrates. Untreated concrete and nature rock used for breakwaters are acceptable.
6. The specimens' shells should be thoroughly rinsed in water at the site to remove mud and debris which are sources of contamination of the tissues inside.

The Department of the Interior protects and manages the nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its special responsibilities to American Indians, Alaska Natives, and affiliated Island Communities.

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